

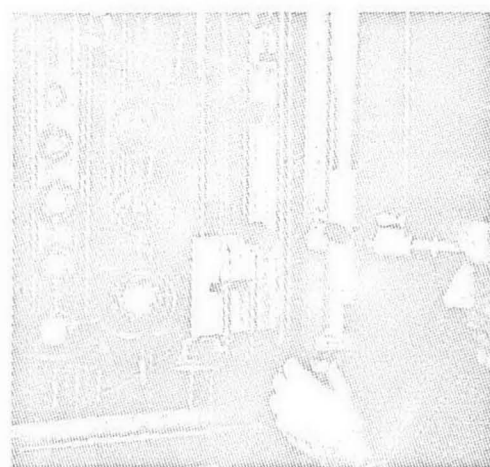
For use at higher pressures, the vessel becomes a heavy-walled metallic container and the measurement of the mass of a gaseous test fluid and the pressure are complicated. A number of investigators, some are listed by Cornings (13), have employed an approach in which the test fluid is charged to the high pressure vessel and its pressure and temperature determined, Figure 1. The mass of the sample is determined afterward by expanding it to atmospheric pressure or below in a large vessel at known temperature. Thus, the mass must be calculated from a second set of P - V - T measurements at conditions for which the density of the material is known with sufficient accuracy.

Several points should be mentioned regarding this method. One approach is to evacuate the system, close V3, Figure 1, inject the sample, close V1, measure the pressure and thermostat temperature, and then close V2. The sample is then expanded from the measured volume of the sample vessel to low pressure in the vessel plus the measured volume of the expansion vessels and the manifold system. It is clear that, for high accuracy, significant difficulty is encountered in determining the volume of the manifolding and knowing its temperature with sufficient accuracy. Further, ideal gas behavior cannot be assumed for the sample at atmospheric pressure (14), as was done by many earlier investigators, for computing the sample mass. The accuracies obtainable with careful work are represented by those of Bennett and Dodge (15), whose es-

timated errors were less than 4:1,000 for the latter compressibilities (PV/P_0V_0) reported. It should also be noted that overcharging of the system yields a single data point.

High pressure systems

A variation (16) of this method has been used by Dakin and Ellington for several years for pressures to 3,000 lb./sq. in. and temperature from -300° to 310°F , Figure 2. This variation has the advantages that the mass of the sample is determined both as it is charged into the high pressure vessel and released from it, and that a single charging yields several data points. In essence, the high pressure and manifold system are evacuated, the vessel immersed in liquid nitrogen, the sample measured at low pressure and passed into the vessel and condensed. Alternately for noncondensables, a high pressure buret is used to measure the sample into the vessel. To conduct a run, the vessel is warmed, the contents stirred, the vessel placed in the thermostat bath, the temperature stabilized and the pressure measured. Then, stabilizations are made at other temperatures and the pressures measured. Since the high pressure capillary system to the pressure gauge separator is also filled with sample, a mass balance must be made to calculate the density of the material in the vessel for each temperature. Then a fraction of the sample is bled into the low pressure buret system and measured, and runs made for the same temperatures as before. As a check on the run series, the mass



Institute of Gas Technology's P-V-T apparatus diagrammed in Figure 13.

charged must equal the sum of the masses bled out of the vessel. Careful work with this relatively unsophisticated system yields densities with errors of less than 1:1,000. Michels, *et al.* (17) quote results accurate to 1:10,000 for a very refined apparatus.

A further variation of the basic method which has been widely used industrially for temperatures near ambient is that evolved by Bean (18, 19), Figure 3. The high pressure vessel A and the expansion volume B are immersed in the same thermostat bath. The expansion volume is relatively small so that numerous expansions (hence data points) are obtained to reduce the vessel pressure to near atmospheric. The industrial unit has been shown to yield densities with errors of less than 1:1,000 (19).

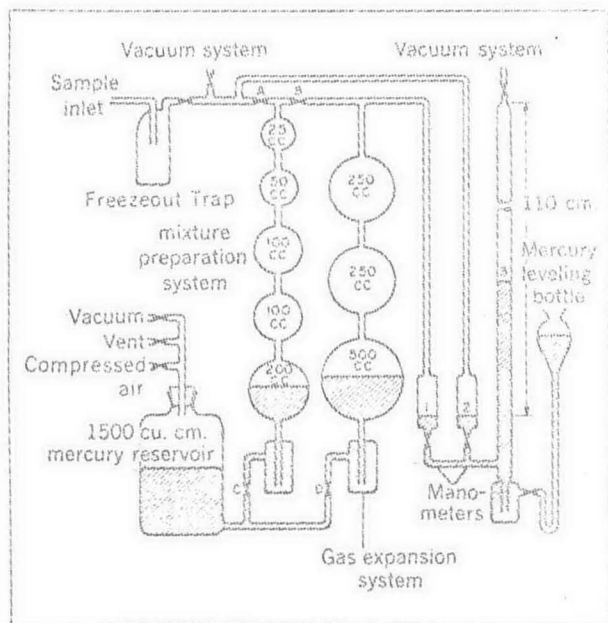


Figure 13. Schematic diagram of low pressure variable-volume apparatus (14).

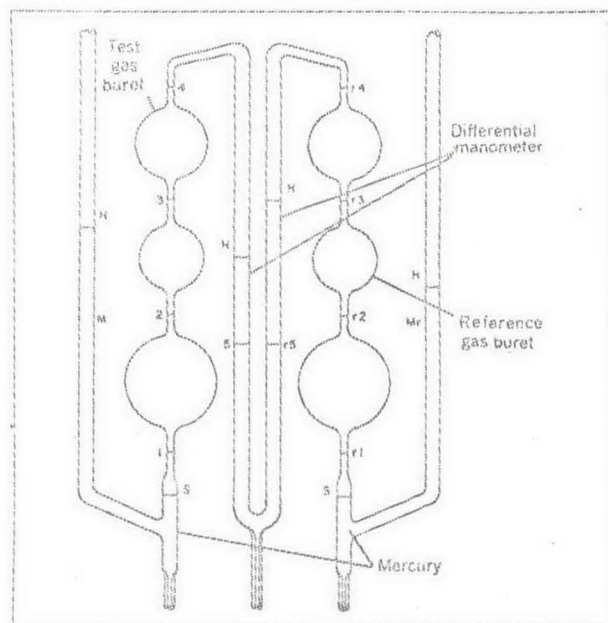


Figure 14. Differential P-V-T apparatus for obtaining second virial coefficients (35).